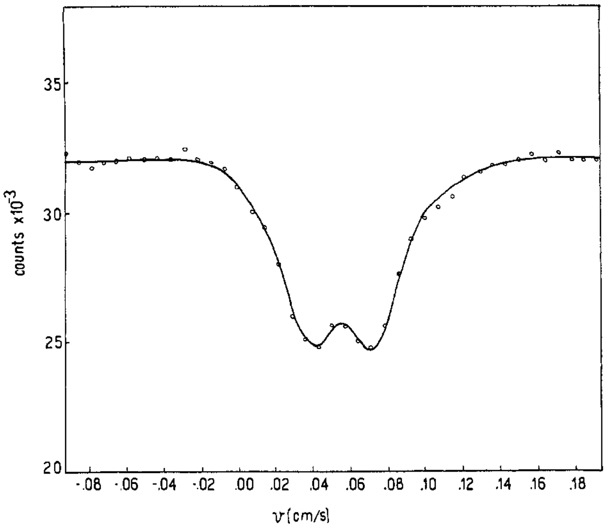

Figure 1.—Mössbauer spectra of iron(III) tris(dimethyldithiocarbamate) at room temperature.

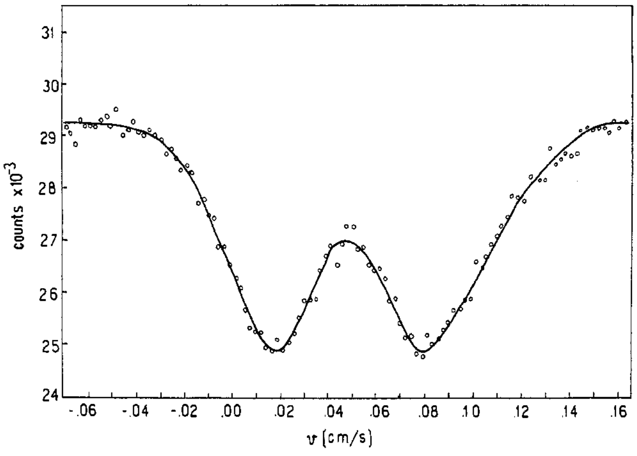

Figure 2.—Mössbauer spectra of iron(III) tris(diisopropyldithiocarbamate) at room temperature.

pole interaction and isomer shift can be correlated with the magnetic properties.

The relationship between magnetic state and quadrupole interaction has been discussed previously by Danon[9] and by Duncan and Golding.[11] Although the complete crystallographic structure of $Fe^{III}(DTC)_3$ has not yet been worked out, there are good reasons to believe[7,8] that each of the bidentate DTC ligands is bonded through its two sulfur atoms so that the resulting point group symmetry at the iron site is D_3. Under the influence of a ligand field of such symmetry the high-spin d^5 complexes have a spherically symmetric configuration which does not contribute to the electric field gradient (EFG) at the iron nucleus. The low-spin d^5 complexes on the other hand have a nonspherical electron distribution which gives rise to an appreciable EFG at the iron nucleus. Since at 300°K all of these complexes contain an equilibrium between the low- and high-spin states one could expect to find a superposition of the Mössbauer-effect spectra of each of the two forms. The fact that this is not observed indicates that the relaxation time to change from one form to the other is much shorter than the lifetime ($\tau = 1.45 \times 10^{-7}$ sec) of the Fe^{57} $I = {}^3/_2$ state and that the nuclei then "see" an average EFG which depends on the contribution of each form in the equilibrium.

Mössbauer spectra taken on the green methyl complex mentioned above show a quadrupole interaction of the order of 0.26 cm/sec in agreement with the results of Wickman and Trozzolo for $ClFe(N,N\text{-dimethyl-}DTC)_2$.[12,13]

With the available data it is not easy to interpret the correlation between magnetic moment and isomer shift. One or both of the following mechanisms could be responsible for it.

(i) The isomer shift in the isopropyl complex is smallest because the bonding between the ligands and the iron is more covalent than in the complexes with higher magnetic moments. This higher degree of covalency in the metal–ligand bond is also responsible for a larger Δ and therefore for a smaller population of the high-spin state.

(ii) There is an intrinsic difference in the isomer shift of each of the magnetic forms of a given complex because the bonding between the DTC ligands and the iron ion in the low- or high-spin configurations is qualitatively different (see ref 10). The observed isomer shift would then be a weighted average between those of each form in equilibrium.

An investigation of the temperature dependence (between 4 and 300°K) of the quadrupole interaction and the isomer shift in these complexes is presently in progress.[16] Preliminary results at temperatures down to 4°K confirm the interpretation given here for the correlation between EFG and magnetic moment. When the temperature is decreased, the quadrupole interaction increases as the population of the low-spin state increases and the magnetic moment decreases as observed by White, *et al.*[7,8] More detailed measurements are necessary to distinguish between the alternative interpretations of the isomer shift data.

Acknowledgment.—It is a pleasure to thank Dr. R. Levitus for valuable advice concerning the preparation and identication of the samples used in this work, Dr. H. H. Wickman for valuable discussions, Professor F. A. Cotton for a critical reading of the manuscript, and Dr. B. B. de Deferrari for some of the elemental analyses.

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CONTRIBUTION FROM THE AMERICAN CYANAMID COMPANY,
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Difluorocyanamide[1]

BY M. D. MEYERS AND S. FRANK

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Several recent papers have described reactions of elemental fluorine in aqueous solution to produce prod-

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ucts containing N–F bonds. Grakauskas[2] first used this aqueous fluorination method to prepare N,N-difluorourea in 70–75% yield. Compounds of the type RNF_2, $HFNCO_2R$, and RFNCONHR (R = alkyl) have also been obtained from the fluorination of dilute solutions of amides, urethanes, and N-substituted ureas,[3] and a solution of N,N-difluorosulfamide was produced when an aqueous solution of sulfamide was fluorinated.[4]

In this note we report the preparation of difluorocyanamide, F_2NCN, by this technique. Fluorination of phosphate-buffered aqueous cyanamide (H_2NCN) solutions produced F_2NCN in yields of about 20% based on fluorine. Optimum yields were obtained with solution temperatures of 5–9°, high gas flow rates (600 cc/min), and *no* mechanical stirring. Deviation from these conditions resulted in lower F_2NCN production and extensive formation of HNF_2 and CO_2. Difluorocyanamide was obtained from the product mixture by fractional codistillation.[5]

Difluorocyanamide is a white solid at $-196°$ and a colorless liquid below its boiling point, $-61°$, determined from vapor pressure measurements. It has been stored as a gas at room temperature in Pyrex glass bulbs for periods up to 2 years with little evidence of decomposition. The molecular weight found by gas density measurements was 76 ± 2 (calcd 78). The mass spectrum shows a major peak corresponding to a CN_2F_2 cation. Mass spectra of fluorocarbons containing a triple bond characteristically show large parent peaks.

The four infrared stretching fundamentals for F_2NCN are given in Table I. The highest frequency fundamental[6] at 2244 cm^{-1} is consistent with the cyanamide structure rather than the possible isomeric carbodiimide, FN=C=NF. Disubstituted carbodiimides have strong absorption at 2150–2100 cm^{-1}.[7] The other fundamentals observed in the 1050–250 cm^{-1} range are also in agreement with the cyanamide structure. A complete infrared study and vibrational analysis has been carried out.[8]

TABLE I

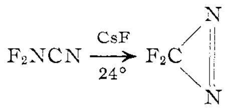
INFRARED STRETCHING FUNDAMENTALS OF F_2NCN VAPOR

Position, cm^{-1}	Assignment	Intensity
2244 (triplet)	—C≡N	Medium
1024 (triplet)	Mainly C—N	Strong
891 (doublet)	Mainly NF_2 asym	Very strong
841 (triplet)	Mainly NF_2 sym	Strong

The F^{19} nmr spectrum showed a single broad band with slight triplet character centered at ϕ -70.5 in $CFCl_3$ solution. This band position is significantly downfield from those found for NF_2 groups attached to carbon in other hydrocarbon and fluorocarbon difluoramino derivatives.[9]

Several experiments with F_2NCN were carried out to explore the possibilities for trimerization or polymerization reactions characteristic of H_2NCN[10] and many other nitriles. Thus, both FCN[11] and ClCN[12] form polymeric products under mild conditions, whereas heat and pressure are required for partial conversion of CF_3CN to the triazine.[13] Little effect was observed when F_2NCN was heated for 16 hr at 120° at a calculated pressure of 7 atm. Difluorocyanamide was also recovered unchanged after storage for 1 month as a liquid at 24° in a sealed Pyrex glass capillary tube.

A unique rearrangement reaction was found to occur in the presence of cesium fluoride to produce the isomeric heterocyclic product, difluorodiazirine



The heterogeneous reaction occurred rapidly and almost quantitatively and provides a convenient preparative route to the diazirine. Difluorodiazirine has been fully characterized recently by Mitsch.[14]

Experimental Section

A Pyrex glass vacuum line was used in the characterization and reactions of F_2NCN. Joints and stopcocks were lubricated with Kel-F No. 90 grease. Pressure measurements were made with mercury manometers and precision low-pressure gauges (obtained from Wallace and Tiernan, Inc., Belleville, N. J.).

Caution!—Difluorocyanamide is a highly explosive compound. It has been manipulated routinely in the vacuum line with liquid nitrogen baths, but adequate shielding and protection must be used.

The handling equipment, procedures, and precautions employed in metering elemental fluorine have been described.[15] Connection from the metal–fluorine handling system to the Pyrex glass reaction flask was made by using a copper ball joint. The fluorine was purchased from the Allied Chemical Co. and the helium from the Matheson Co.

Preparation of F_2NCN.—A slurry of 13 g of $Na_2HPO_4 \cdot 7H_2O$, 20 g of $NaH_2PO_4 \cdot H_2O$ (J. T. Baker reagents), and 20 ml of deionized water was mixed with 70 ml of a 50% aqueous cyanamide solution[16] at 5°. The mixture was poured into a 300-ml single-neck (₸ 24/40) round-bottom flask surrounded by an ice bath. The flask was fitted with a gas inlet tube extending 3 cm below the surface of the liquid. An exit tube above the liquid surface led downstream to four cold traps (two at $-78°$ and two at $-196°$) connected in series for isolation of the volatile fluorination products. The traps, 30 cm long and 4.5 cm in diameter,

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were connected with S_J 18/9 ball joints. An exit bubbler filled with Kel-F oil was connected to the last trap. The entire apparatus was situated in a well-ventilated walk-in hood behind a transparent safety shield.

A gas stream consisting of a mixture of helium (550 cc/min) and fluorine (30 cc/min) was passed through the system. Periodically, the gas stream was diverted and passed through an infrared gas cell by means of a tee and stopcock in the line between the two traps at −78°. The infrared spectra showed weak bands due to F_2NCN and CO_2. The solution became yellowish and then dark orange as the run progressed. During the fluorination, the infrared spectra of the product stream indicated a steadily increasing amount of CO_2 and a relatively constant F_2NCN concentration. After 1 hr, the gas stream was stopped, the fluorinated solution emptied, and the flask recharged with fresh reagents. Fluorination was continued for another hour. The water bath surrounding the reaction flask was held between 9 and 12° by adding ice.

Isolation of the material retained in the two −196° traps by vacuum line techniques yielded 14 mmoles of crude product. Infrared spectra of this product indicated that the composition was approximately 65% F_2NCN, 30% CO_2, and 5% other species. The molecular weight (gas density) of the mixture was 69. Preparative fractional codistillation was employed to isolate 7.5 mmoles of pure F_2NCN from the total crude product. Other species in the crude product, in addition to CO_2, were isolated by fractional codistillation and identified by infrared spectra: HCN, N_2F_4, HNF_2, HNCO, and N_2O.

Infrared Spectra.—The infrared data given in Table I were obtained with a Perkin-Elmer 521 grating infrared spectrophotometer. A Micro-Gas cell[17] was used, with a 10-cm path length and KBr windows. The cell was equipped with a Hoke 440 series stainless steel bellows valve and a stainless steel ball joint for connection to the vacuum line. Other spectra were obtained with a Perkin-Elmer Model 137B instrument.

Nmr Spectrum.—A Varian V4300B high-resolution nuclear magnetic resonance spectrometer operating at 56.4 Mc was used. Several different samples of F_2NCN were examined in *ca.* 10% solutions of $CFCl_3$ at 30°. The ϕ value given is the chemical shift in ppm relative to $CFCl_3$ as an internal standard.

Mass Spectrum.—The mass spectrum of F_2NCN was obtained with a Consolidated Electrodynamics instrument (Model 21-103) with the inlet at room temperature. Partial decomposition occurred with the inlet at 150°. An ionizing voltage of 70 v was used. The spectrum had the following characteristics (mass, ion, relative intensity): 31, CF, 100; 59, CN_2F, 88.7; 78, CN_2F_2, 81.3; 33, NF, 47.8; 26, CN, 24.5; 40, CN_2, 24.0; 14, N, 20.4; 52, NF_2, 12.6; 64, CNF_2, 3.9; 50, CF_2, 3.2.

Vapor Pressure.—Vapor pressures were measured on a freshly codistilled sample of F_2NCN with a simple U-tube Hg manometer. The manometer was isolated from the vacuum line with a Fisher Porter Co. needle valve (1.25 mm, Teflon plastic stem) giving a grease-free vapor space. Some observed pressures were: −93.5°, 98 mm; −78°, 282 mm; and −75°, 340 mm. Extrapolation of the log p_{mm} *vs.* $1/T$ plot resulted in a normal boiling point of $-61 \pm 1°$. The straight-line relationship fits the equation $\log p_{mm} = -1075/T + 7.97$. This equation gave a heat of vaporization of 4900 cal/mole and a Trouton's constant of 23.

Ultraviolet Spectrum of F_2NCN.—The gas phase spectrum obtained on a Cary Model 14 instrument showed a gradually increasing absorption toward the end of the measurable region in air. The absorbance at 262 mμ was calculated to be 1.0 at 760 mm in a 10-cm cell.

Rearrangement of F_2NCN to Difluorodiazirine.—A glass sample bulb, 10 cc in volume, was charged in a drybox with 1 g of CsF (American Potash and Chemical Corp.). The reactor was evacuated and warmed briefly with a heat gun. A 200-mm sample of F_2NCN was admitted and the mixture was allowed to stand for 75 min at 24°. After this period, the total pressure found in the reactor was 185 mm; less than 10 mm of the gas was not condensed at −196°. Infrared examination of the material condensed at −196° showed only difluorodiazirine.[14] Fractional codistillation of this product confirmed the presence of a single major component.

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(17) Barnes Engineering Co., Instrument Division, Stamford, Conn.

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A Phosphine Derivative of Triiron Dodecacarbonyl

BY ROBERT J. ANGELICI AND E. EDWIN SIEFERT

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Since the original formulation of triiron dodecacarbonyl in 1930,[1] the structure of this molecule has been investigated by a variety of techniques, but with limited success. Because of disorder in crystalline $Fe_3(CO)_{12}$,[2] the usual structural proof by X-ray methods was unfortunately not possible. Recently, however, Dahl and Blount,[3] on the basis of their X-ray investigation of $[HFe_3(CO)_{11}]^-$, suggested that the structure of $Fe_3(CO)_{12}$ consists of a triangular arrangement of the iron atoms. Two iron atoms, each bonding three terminal CO groups, are bridged by two CO groups, while the unique iron atom is bonded to four terminal CO groups. The postulated structure, however, depends on a close similarity between the molecular structures of $[HFe_3(CO)_{11}]^-$ and $Fe_3(CO)_{12}$. Such a similarity is suggested by Mössbauer studies of these compounds.[4]

In an attempt to resolve the structural problem, we have prepared a simple phosphine derivative of triiron dodecacarbonyl, $Fe_3(CO)_{11}P(C_6H_5)_3$, having properties very similar to those of its parent. Presumably, their molecular structures are also basically the same.

Experimental Section

Preparation of $Fe_3(CO)_{11}P(C_6H_5)_3$.—Approximately 50 g of $Fe_3(CO)_{12}$[5] and 25 g of $P(C_6H_5)_3$ dissolved in 500 ml of $CHCl_3$ were allowed to react at 45° for 45 min under nitrogen. After cooling to −72°, the solution was allowed to warm to room temperature under vacuum, during which time the $CHCl_3$ and $Fe(CO)_5$ distilled from the mixture. The solid residue was extracted with successively smaller portions (500, 250, 150, 100, and 100 ml) of CCl_4, leaving much of the $P(C_6H_5)_3$, $Fe_3(CO)_{12}$, $Fe(CO)_4P(C_6H_5)_3$, and $Fe(CO)_3[P(C_6H_5)_3]_2$ undissolved. The

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